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Optimal design of biodiesel production process from waste cooking palm oil

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Abstract

A design methodology for biodiesel production from waste cooking palm oil is proposed. The proposed method is flexible to the biodiesel process using various catalyst types: alkali and acid catalyst in homogenous and heterogeneous forms, and different process: enzyme process and supercritical process. A two-step approach of hydrolysis and esterification processes is also considered. Waste cooking palm oil consists of a mixture of triglyceride (e.g., trilaurin, tripalmitin, triolein, tristearin, trilinolein and trilinolenin) and free fatty acids (e.g., lauric acid, palmitic acid, stearic acid, oleic acid, linoleic and linolenic acid). A driving force approach and thermodynamic insight are employed to design separation units (e.g., flash separator and distillation) minimizing the energy consumption. Steady-state simulations of the developed biodiesel processes are performed and economic analysis is used to find a suitable biodiesel process. The results show that based on a net present value, the heterogeneous acid catalyzed process is the best process for biodiesel production. With the design methodology, the proposed biodiesel process can save the energy requirement of 41.5 %, compared with a conventional process.

Keywords: Process design; biodiesel production; waste cooking palm oil; superstructure

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1. Introduction

Due to a limited availability of fossil fuels and an increased price of petroleum diesel, biodiesel, known as a fatty acid alkyl ester, has become an important alternative fuel that offers several advantages including its renewability and low emission profile of carbon monoxide and unburned carbon. Biodiesel production using an alkali catalyst is a common way due to its low temperature and pressure operation. However, alkali catalyst is quite sensitive to free fatty acid in biodiesel feedstock and thus, expensive pure vegetable oil, which contains free fatty acid of lower than 1 wt.%, is required [1].

In the case of using vegetable oils with high content of free fatty acid, an esterification process based on acid catalyst can be applied to eliminate free fatty acid before further processing via the conventional transesterification process. Presently, a number of biodiesel processes have been developed. Zhange et al. [2] proposed four biodiesel plant flowsheets such as alkali catalyzed process, acid catalyzed process and two-step catalyzed process. West et al. [3] investigated the biodiesel production from waste cooking oil using the supercritical condition of methanol and heterogeneous acid catalyst. Marchetti et al. [4] studied a two-stage transesterification process for producing biodiesel in the presence of different catalysts. Lee et al. [5] analyzed the performance of the plug flow reactor under the methanol supercritical condition to produce biodiesel. Another interesting biodiesel process involves a hydrolysis of triglyceride in vegetable oil to fatty acid. All the fatty acid produced is further processed via an esterification process [6].

Apart from the development of biodiesel processes, an economic analysis is also important to prove a feasibility of the developed process. The best alternative process for biodiesel production should be determined by considering profitability indicators such as a net profit, return on investment and net present value [2]. Jegannaraan et al. [7] indicated that although the enzyme catalyzed process shows a better performance for biodiesel production, the alkali catalyzed process is the best process regarding the manufacturing cost. Lim et al. [8] found that biodiesel production from the supercritical methanol process is better than the alkali catalyzed process because of a higher byproduct, glycerol, is generated. West et al. [3] analyzed various biodiesel processes and showed that the heterogeneous acid catalyzed process is the most feasible option because of the highest net annual profit. Kiss et al. [9] compared the capital cost of homogeneous and heterogeneous catalyzed processes. The sensitivity analysis of utility costs on glycerol price was performed without consideration of time value of money and change in raw material and product prices.

In general, pure refined vegetable oils are used as feedstock for biodiesel production; however, their price highly increases a biodiesel production cost. Alternatively, use of waste cooking oil with a lower cost seems to be an attractive option [10]. The objective of this study is to propose a design methodology for a biodiesel production from waste cooking palm oil, which contains 10 wt.% of free fatty acid. A thermodynamic insight and a driving force technique [11] are used to design the biodiesel process. The proposed methodology is flexible to biodiesel production using various catalysts: alkali and acid catalysts in both the homogenous and heterogeneous forms, and different processes: enzyme process and supercritical process. The production of biodiesel based on a two-step approach: hydrolysis of triglyceride followed by esterification of free fatty acid, is also considered. Economic assessment of biodiesel production with different processes is compared in terms of economic criteria such as net profit, return on investment (ROI), net present value (NPV), break-even price of biodiesel. The best process is determined with respect to the highest net present value and the lowest energy consumption.

2. Biodiesel production from waste cooking oil

The main reaction for biodiesel production consists of the three-step transesterification of triglyceride, diglyceride and monoglyceride with methanol as shown in Eq. (1).

Table 1. Operating conditions and performance of the reactor using different catalysts

Catalyst	T (°C)	P (atm)	Conversion (%)
NaOH (base cat.) [12]	60	1	94.3
H_2SO_4 (acid cat.) [13]	130	1	90
KOH/Al_2O_3 (heterogeneous base cat.) [14]	70	1	91.7
DTPA/Clay (heterogeneous acid cat.) [15]	70	17	94
κ-Carrageenan (enzyme process) [7]	30	1	99
Supercritical methanol [16]	350	40	95
Lipase (hydrolysis process) [6]	45	1	95

$$\begin{aligned} &\text{Triglyceride} + CH_3OH \xleftrightarrow{k_1 \text{ and } k_2} \text{Diglyceride} + RCOOCH_3 \\ &\text{Diglyceride} + CH_3OH \xleftrightarrow{k_3 \text{ and } k_4} \text{Monoglyceride} + RCOOCH_3 \\ &\text{Monoglyceride} + CH_3OH \xleftrightarrow{k_5 \text{ and } k_6} \text{Glycerol} + RCOOCH_3 \end{aligned} \quad (1)$$

In general, a vegetable oil contains typically mixed triglycerides with different fatty acids, which vary with a number of carbons and unsaturated bonds. For palm oil, the percentage of lauric acid, myristic acid, palmitic acid, stearic acid oleic acid, lineleic acid, and linolenin acid are 0.1, 0.1, 10.2, 3.7, 22.8, 53.7 and 8.6, respectively. Therefore, a mixture of triglycerides consists of trilaurin, trimyristin, tripalmitin, tristearin, triolein, trilinolein and trilinolenin is assumed to represent the triglycerides in palm oil, whereas lauric acid, palmitic acid, stearic acid, oleic acid, linoleic and linolenic acid are assumed to be free fatty acids in a waste cooking palm oil. When an esterification is applied to reduce free fatty acids in waste cooking oil, the following reaction is occurred.

$$RCOOH + CH_3OH \leftrightarrow RCOOCH_3 + H_2O \quad (2)$$

Simulation of biodiesel production is performing using process simulator, Hysys. All the triglycerides and free fatty acids mentioned above are defined using a “Hypo manager” tool. In this study, a waste cooking palm oil containing 10 wt.% of free fatty acids at the flow rate of 46.33 kmol/h is used as feedstock for biodiesel production. The design target is to obtain the biodiesel product with the purity of 99.5 wt.%. Seven process alternatives for biodiesel production based on alkali catalyst, acid catalyst, solid base catalyst, solid acid catalyst, enzyme catalyst, supercritical methanol and two-step process of hydrolysis and esterification are considered.

3. Design methodology

A design methodology for biodiesel production processes is proposed based on a thermodynamic insight method [11]. Chemical and physical properties of the chemicals present in the system are used to select separation techniques and thus, the first step is to collect relevant data such as chemical formula, molecular weight, normal boiling point, freezing point, liquid density, water solubility, critical properties, azeotrope of a mixture and types of catalysts. Then, the binary ratio of each property for all components is computed to select the feasible separation techniques such as a flash operator, distillation column, decanter and adsorption. As a result, a generic superstructure of process alternatives of all biodiesel production process is generated. Rigorous steady-state process simulations are performed for their performance analysis and economic evaluation. In the process simulation step, the UNIQUAC model is used for phase equilibrium calculations, while the percentage of recoveries for flash separators and

distillations are specified at 90% and 99%, respectively. The driving force technique is used to design distillation columns minimizing the energy consumption and total capital cost. Based on the reverse approach, a number of stages and feed location that matches the driving force target are determined. It is noted that in the reaction section of each biodiesel process alternative, a conversion reactor is assumed. Table 1 summarizes the operating conditions and oil conversion of the reactor reported in literatures.

4. Results and discussion

4.1. Process design

Fig. 1 shows the superstructure of the proposed biodiesel production process from waste cooking palm oil with different types of catalyst. In the figure, the variable Y_i is varied, depending on the available streams; when the value Y_i is equal to one, such a stream has to be considered. This means that when Y_1 and Y_4 are available streams, the alkali catalyzed process is a preferable option, whereas the acid catalyzed process, heterogeneous catalyzed process, enzyme catalyzed process and supercritical methanol process are involved if Y_2 and Y_5 exist. A pretreatment reactor is used to reduce free fatty acids when alkali catalyst is used as catalyst in the main reactor.

In a conventional biodiesel process, an excess methanol is recovered by using a distillation column and a by-product glycerol is separated from biodiesel by a decanter. The product biodiesel is first purified by using a distillation with partial condenser and then a neutralization reactor is employed to remove the remaining homogenous catalyst. Based on the thermodynamic insight analysis of all components in the biodiesel production process, a new designed process is proposed. To recover the excess methanol in crude biodiesel product, a flash column is chosen; water and methyl laurate are the light and heavy key components. The light key product is sent to a distillation column in order to separate methanol and water and then the recovered methanol from the column is recycled to the biodiesel production process. The heavy key product from the flash separation consists of mostly biodiesel, glycerol and unreacted mixed triglyceride. From the ternary phase diagram for methyl oleate (a representative of mixed methyl esters), methanol, glycerol system (Fig. 2), two liquid phase region is observed, which implies that the mixed methyl ester can dissolve in glycerol. Therefore, the heavy product of the flash column is sent to a decanter to separate a light phase component (e.g., mixed methyl ester and methanol) from a heavy phase component (e.g., water, glycerol and methanol). The second and third distillation columns are used for further purification of mixed methyl esters from methanol and mixed triglycerides, respectively.

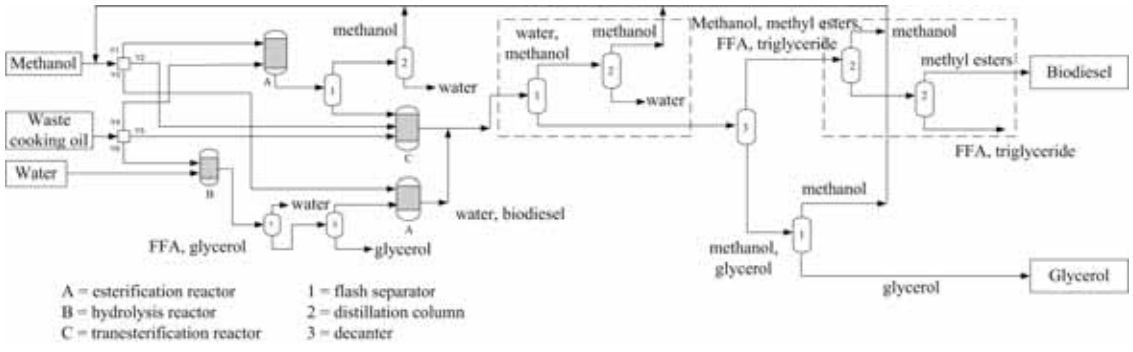

Fig. 1. Superstructure of the proposed biodiesel process

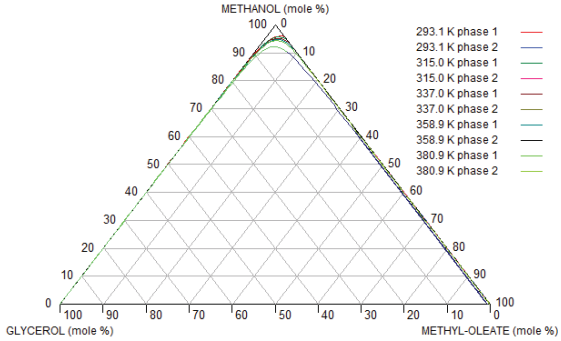

Fig. 2. Ternary phase diagram of the system of methyl oleate, methanol and glycerol

Table 2. Raw material prices [17]

Oil	0.75$/kg	Biodiesel	1.07$/L	Sulfonic acid/clay	0.6$/kg
Methanol	0.56$/kg	Glycerol	10$/kg	*κ*-Carrageenan	10$/kg
Steam	0.0088$/kg	NaOH	0.6$/kg	Lipase	1.5$/kg
Cooling water	0.013$/kg	H_2SO_4	0.6$/kg		
Electricity	0.04$/kW-h	KOH/Al_2O_3	19.8$/kg		

4.2. Economic analysis

In this section, steady-state simulations of the proposed biodiesel processes are performed for process economic analysis in terms of a total investment cost, total production cost and profitability in order to determine the best economically feasible process. The prices of raw materials used for the economic evaluation are listed in Table 2. Table 3 shows the total investment cost of the new design processes, compared with conventional ones, for the production of biodiesel using different catalysts. The results show that the fixed capital cost of distillation columns for methanol recovery and biodiesel purification in the heterogeneous acid catalyzed process and supercritical process show the highest value because a large amount of methanol is required for the transesterification reactor. In addition, size of the reactors and distillations are larger than other processes, causing the highest total investment cost. In contrast, the alkali catalyzed process has the lowest total investment cost due to the requirement of a lower feed ratio of methanol to oil. Due to a high pressure operation, the equipment cost (i.e., reactor, pump and distillation) for the heterogeneous acid catalyzed and supercritical methanol processes are very high. The total production cost and economic factors (i.e., net profit and net present values) of the conventional and proposed new design biodiesel proposes are compared in Table 4. It indicates the dependence of the production cost on the prices of raw material and catalyst as well as the utility cost. Although the enzyme catalyzed process has the highest productivity, a high cost of enzyme results in less profit, compared with other processes. When considering the return on investment regardless a project life year, the alkali catalyzed process shows the best alternative. A net present value (NPV) is another key indicator that should be considered to find an economically feasible process. It is found that among the alternative processes, the heterogeneous acid catalyzed process shows the highest NPV as its net profit is the highest. Fig. 3(a) compares costs of the total investment, raw material, revenue, NPV and utility (i.e., steam and cooling) between the conventional and new proposed biodiesel process based on a heterogeneous acid catalyst. With the proposed design methodology, the new developed biodiesel process requires a lower energy consumption (41.7% energy saving), leading to a lower operating cost and thus NPV. The cash

flow analysis shown in Fig. 3(b) indicates that all the proposed biodiesel processes are economically feasible.

Table 3. Capital costs of biodiesel production (A = new design process and B = conventional process)

	Alkali process		Acid process		Solid base process		Solid acid process		Enzyme process		Supercritical process		Two-step process	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Pretreatment reactor ($x10^6$)	3.95	3.9	-	-	3.94	3.9	-	-	-	-	-	-	-	-
Main reactor ($x10^6$)	0.605	0.605	3.9	3.9	1.47	1.47	2.86	2.86	2.93	2.93	1.45	1.45	0.605	0.605
Neutralization reactor	3.83	3.83	3.83	3.83	3.83	3.83	-	-	-	-	-	-	-	-
Heater ($x10^5$)	1.2	2.84	0.6	2.12	1.83	2.84	0.753	2.11	0.72	2.13	0.17	1.78	0.625	2.67
Cooler ($x10^5$)	0.478	7.14	0.4	-	0.402	7.14	0.983	3.44	0.484	3.29	1.58	4.61	0.586	-
Pump ($x10^6$)	-	-	-	-	-	-	0.108	0.108	-	-	1.2	1.2	-	-
Decanter ($x10^6$)	0.73	1.43	1.5	1	1.69	1.43	2.49	1.43	2.02	0.571	3.59	2.12	2.02	0.62
Flash ($x10^6$)	0.45	-	0.3	-	1.56	-	0.605	-	0.3	-	1.75	-	0.39	-
Distillation I for methanol recovery ($x10^6$)	0.324	1.41	-	-	0.4	1.35	1.51	-	1.15	-	4.14	-	1	-
Distillation II for methanol recovery ($x10^6$)	0.4	1.18	0.3	1.76	0.153	2.71	0.425	2	0.3	1.07	0.41	1.76	-	1.40
Distillation for glycerol separation ($x10^6$)	-	1.46	-	1.20	-	0.607	-	0.628	-	0.636	-	0.666	-	0.847
Distillation for methanol separation from biodiesel ($x10^6$)	1	-	1	-	0.955	-	1.33	-	0.93	-	1.4	-	1.22	-
Distillation for biodiesel purification ($x10^6$)	2.3	3.53	3	3.97	3.02	4.19	2.41	4.50	2.57	4.21	2.55	5.24	3.17	5.23
Total bare module cost($x10^7$)	0.856	1.17	1.1	1.2	1.2	1.42	1.35	1.37	1.14	1.1	1.73	1.16	0.969	0.99
Contingency fee ($x10^6$)	1.55	2.1	2.0	2.16	2.15	2.56	2.44	2.46	2.05	1.98	3.11	2.1	1.74	1.78
Auxillary cost ($x10^6$)	2.58	3.5	3.4	3.6	3.59	4.27	4.06	4.1	3.42	3.31	5.18	3.49	2.91	2.97
Fixed capital cost ($x10^7$)	1.27	1.72	1.6	1.77	1.77	2.11	2.00	2.02	1.64	1.63	2.55	1.72	1.43	1.47
Working capital cost ($x10^6$)	1.91	2.59	2.5	2.66	2.65	3.16	3.01	3.03	2.53	2.45	3.83	2.59	2.16	2.2
Total investment cost ($x10^7$)	1.46	1.98	1.9	2.04	2.04	2.42	2.31	2.33	1.94	1.88	2.94	1.98	1.65	1.69

Table 4. Total production cost and economic indicators (A = new design process and B = conventional process)

	Alkali process		Acid process		Solid base process		Solid acid process		Enzyme process		Supercritical process		Two-step process	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Oil feedstock ($x10^8$)	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67	2.67
Methanol ($x10^8$)	0.239	0.381	1.3	1.43	0.23	0.185	0.202	0.25	0.376	0.252	0.39	0.39	0.205	0.436
Steam ($x10^6$)	3.03	4.07	3.53	4.98	5.06	6.53	3.48	5.99	2.81	4.16	9.43	9.23	3.09	4.7
Cooling water ($x10^7$)	5.57	9.54	6.92	6.57	6.92	13.6	12.5	14.7	7.53	7.15	34.4	16.8	9.86	9.63
Labor ($x10^6$)	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91
Supervisory ($x10^5$)	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91
Catalyst and solvent ($x10^6$)	4.72	4.72	9.47	9.47	0.028	0.028	0.59	0.59	66.6	66.6	0	0	53.3	53.3
Maintainance ($x10^6$)	0.679	0.907	1.21	1.26	1.01	1.16	1.27	1.21	1.22	1.15	1.23	0.971	0.779	0.771
Laboratory ($x10^5$)	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91
Local tax ($x10^5$)	1.36	1.81	2.42	2.49	2.03	2.34	2.55	2.43	2.44	2.38	2.45	1.94	1.56	1.54
Insurance ($x10^6$)	0.679	0.907	1.21	1.26	1.01	1.16	1.27	1.21	1.22	1.15	1.23	0.971	0.779	0.771
Plant overhead ($x10^6$)	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96
General expense ($x10^5$)	7.82	7.82	7.82	7.82	7.82	7.82	7.82	7.82	7.82	7.82	7.82	7.82	7.82	7.82
Total production cost ($x10^8$)	3.07	4.18	4.2	5.05	3.05	4.38	3.01	4.55	3.84	4.44	3.26	4.92	3.53	4.74
Depreciation ($x10^6$)	0.78	1.04	1.39	1.43	1.16	1.33	1.47	1.4	1.4	1.38	1.41	1.02	0.89	0.885
Revenue ($x10^8$)	6.13	7.02	6.36	6.41	6.37	6.83	6.75	7.25	7.05	7.56	6.62	7.5	6.93	7.29
Net profit ($x10^8$)	3.05	2.82	2.16	1.36	3.3	2.35	3.71	3.04	3.2	3.29	3.34	0.47	3.39	2.54
ROI	21.79	14.2	11.73	6.64	16.78	9.7	16.61	13.074	17	17.53	11.7	2.4	21.45	15.05
NPV before tax ($x10^9$)	1.9	1.75	1.31	0.883	2.05	1.45	2.3	1.89	1.99	2.04	2.07	0.284	2.11	1.58

4.3. Sensitivity analysis

In this section, the sensitivity analysis of the proposed biodiesel processes is studied to determine the effect of key parameters such as oil feed price, biodiesel price and glycerol price on NPV. The price is varied 10%, 20%, 30%, 40% from its original value. The project life of 20 years is assumed. Figs. 4(a)-(c) show that the NPV of the biodiesel process is linearly related to the prices of oil feed, biodiesel and glycerol. The NPV decreases with increasing the oil feed price that affects the total production cost, whereas it increases with increasing the biodiesel and glycerol prices due to an increasing in the revenue.

Biodiesel production based on the enzyme process is more sensitive to the biodiesel price than other processes. Due to its highest of net profit, the heterogeneous acid catalyzed biodiesel process show the maximum NPV.

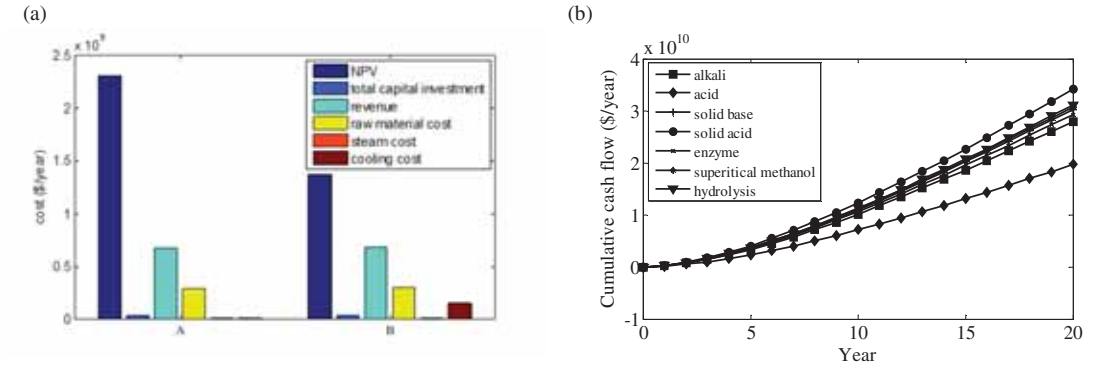

Fig. 3. (a) Cost comparison of the new design (A) and conventional (B) processes for biodiesel production using solid acid catalyst; (b) Cash flow of biodiesel production processes using the proposed design methodology

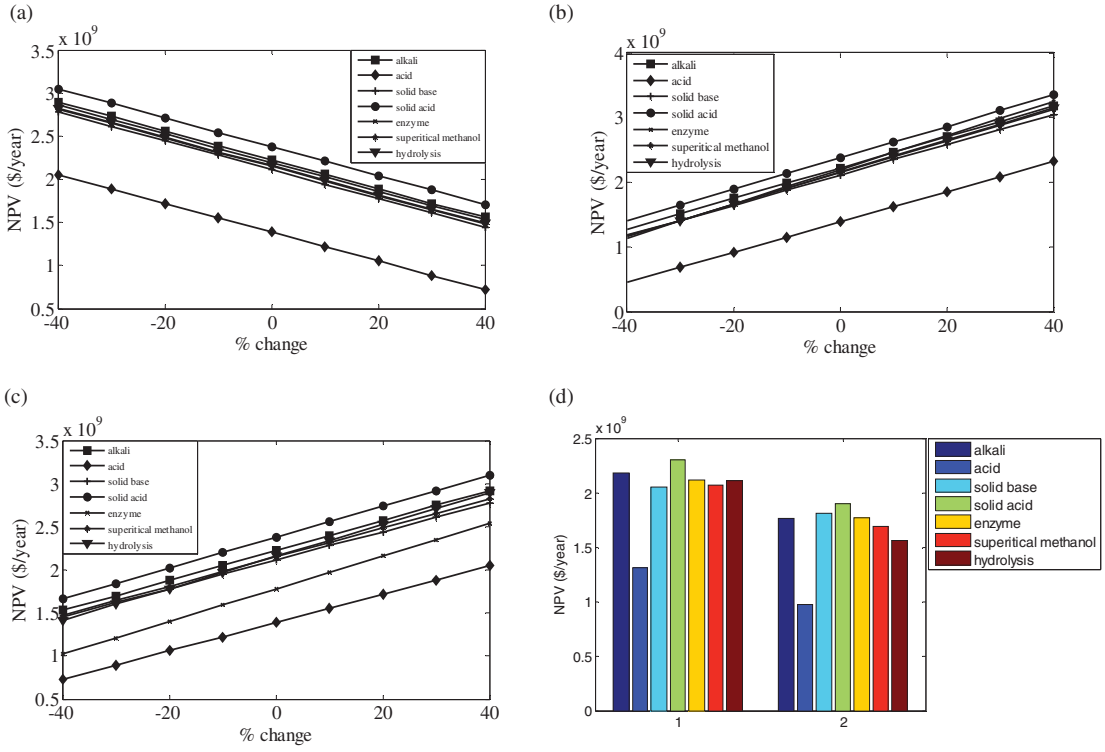

Fig. 4. (a) Effect of oil feed price on the NPV of biodiesel processes; (b) Effect of biodiesel price on the NPV of biodiesel processes; (c) Effect of glycerol price on the NPV of biodiesel processes; (d) Effect of using waste cooking (1) and crude (2) palm oil on the NPV of biodiesel production

Since the fraction of free fatty acid in palm oil affects the raw material cost and thus the production cost, its effect on the NPV of biodiesel process is investigated. Fig. 4(d) compares the NPV of biodiesel process when crude and waste cooking palm oils with different contents of free fatty acid, 5 wt.% and 10 wt.%, are used. When the crude palm oil is used as feedstock, the productivity and the methanol requirement is decreased. Although the energy consumption of biodiesel production using crude palm oil decreases, the NPV of biodiesel production using crude palm oil is still lower than that using waste cooking palm oil. This is because the price of crude palm oil is high while the revenue is low. For both cases, the heterogeneous acid catalyzed process is the best process. It is noted that when the content of free fatty acids in palm oil increases, the size of distillation columns for separating methanol from water is larger because more water is generated from the esterification of free fatty acid. However, the size of equipments does not significantly affect the NPV because the capital cost is lower than the production cost.

5. Conclusions

This study proposed a new design processes for biodiesel production using several types of catalysts such as alkali catalyst, acid catalyst, heterogeneous base catalyst, heterogeneous acid catalyst and enzyme, In addition, the production of biodiesel based on a supercritical methanol process and a two-step approach of hydrolysis and esterification processes was also considered. Waste cooking palm oil containing 10 wt.% of mixed free fatty acids was used as feedstock. The proposed design methodology based on a thermodynamic insight and a driving force technique was employed to design the biodiesel processes. Economic analysis in terms of a net present value, total production cost, total investment cost and return on investment was performed to confirm that new design processes is feasible. The results of the net present value showed that the heterogeneous acid catalyzed process is the economically feasible process even its capital cost is high.

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References

[1] You Y, Shie J, Chang C, Huang S, Pai C, Yu Y, Chang C. Economic Cost Analysis of Biodiesel Production: Case in Soybean Oil. *Energy Fuels* 2007;**22**:182–9.

[2] Zhang Y, Dube MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. *Bioresour Tech* 2003;**90**:229–40.

[3] West A, Posarac D, Ellis N. Assessment of four biodiesel production processes using HYSYS.Plant. *Bioresour Tech* 2008;**99**:6587–601.

[4] Marchetti JM, Miguel VU, Errazu AF. Techno-economic study of different alternatives for biodiesel production. *Fuel Process Tech* 2008;**89**:740–8.

[5] Lee S, Posarac D, Ellis N. Process simulation and economic analysis of biodiesel production processes using fresh and waste vegetable oil and supercritical methanol. *Chem Eng Res Des* 2011;**89**:2626–42.

[6] Serri NA, Kamarudin AH, Abdul Rahaman SN. Preliminary Studies for Production of Fatty Acids from Hydrolysis of Cooking Palm Oil Using *C. rugosa* Lipase. *J Phys Sci* 2008;**19**:79–88.

[7] Jegannathan K, Seng C, Ravindra P. Economic assessment of biodiesel production: Comparison of alkali and biocatalyst processes. *Renew Sust Energy Rev* 2011;**15**:745–51.

[8] Lim Y, Lee H, Lee Y, Han C. Design and Economic Analysis of the Process for Biodiesel Fuel Production from Transesterificated Rapeseed Oil Using Supercritical Methanol. *Ind Eng Chem Res* 2009;**48**:5370–8.

[9] Kiss FE, Jovanović M, Bošković GC. Economic and ecological aspects of biodiesel production over homogeneous and heterogeneous catalysts. *Fuel Process Tech* 2010;**91**:1316–20.

[10] Canakci M, Gerpen JV. Biodiesel production from oils and fats with high free fatty acids. *Trans ASAE* 2001;**44**:1429–36.

[11] Jaksland C, Gani R. Lien K. Separation process design and synthesis based on thermodynamic insights. *Chem Eng Sci* 1995;**50**:511–30.

[12] Narva´ez PC, Rinco´n SM, Sa´nchez FJ. Kinetics of Palm Oil Methanolysis, *J Am Oil Chem Soc* 2007;**84**:971–7.

[13] Wang Y, Ou S, Liu P, Xue F, Tang S. Comparison of two different processes to synthesize biodiesel by waste cooking oil. *J Mol Catal A: Chem* 2006;**252**:107–12.

[14] Noiroj K, Intarapong P, Luengnaruemitchai A, Jai-In Samai. Comparative study of KOH/Al_2O_3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. *Renew Energy* 2009;**34**: 1145–50.

[15] Bokade VV, Yadav GD. Transesterification of edible and nonedible vegetable oils with alcohols over heteropolyacids supported on acid-treated clay. *Ind Eng Chem Res* 2009;**48**:9408–15.

[16] Song E, Lim J, Lee H, Lee Y. Transesterification of RBD palm oil using supercritical methanol. *J Supercrit Fluids* 2008; **44**:356–63.

[17] Seider D, Seader JD, Lewin DR. *Product and process design principles: synthesis, analysis, and evaluation.* New York: Wiley; 2004.